

# PATENT SPECIFICATION

(11) 523 957

1 523 957

- (21) Application No. 24448/76 (22) Filed 12 Jun. 1976  
(23) Complete Specification Filed 30 May 1977  
(44) Complete Specification Published 6 Sep. 1978  
(51) INT CL<sup>2</sup> C11D 17/00  
(C11D 17/00 1/72 1/74 3/04 3/06 3/12  
3/37 3/065)  
(52) Index at Acceptance  
CSD 6A5A 6A5C 6A5D2 6A5F 6A9 6B12P  
6B13 6B14  
(72) Inventor: Stanley Douglas Dickinson

(19)



## (54) COMPOSITIONS CONTAINING FOAM CONTROL SUBSTANCE

(71) We, DOW CORNING LIMITED, a British Company of 12 Whitehall, London, SW1A 2DZ do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:-

This invention relates to detergent compositions containing a silicone foam controlling agent.

The use of solid detergent compositions in the laundering of soiled fabrics is now well-known and widely practised.

Compositions of this type can however give rise to excessive foaming during the wash cycle, particularly when employed in automatic washing machines. Such excessive foaming is objectionable in that it interferes with the efficient laundering of the fabrics and causes overflowing and flooding of the machine.

One method of overcoming this problem is proposed in U.K. Patent No. 1,378,874 which relates to a foam control substance comprising powdered or granular sodium tripolyphosphate having on its surface an organopolysiloxane antifoam. Such foam control substances can be incorporated into powdered or granular detergent compositions and are effective in reducing or suppressing the foaming of aqueous wash liquors in which the detergent is employed. It has, however, been found that such foam control substances lose some of their effectiveness when incorporated into certain detergent compositions, especially those with a high anionic surfactant content, which are subsequently stored for prolonged periods.

We have now found that the loss of effectiveness of foam control substances of the type described can be reduced if the silicone antifoam is at least partially enclosed within a mixture of a water-insoluble wax and a water-insoluble emulsifying agent. Accordingly the present invention provides a powdered or granular detergent composition containing from 0.5 to 20% by weight of a foam control substance which comprises powdered or granular sodium tripolyphosphate, sodium sulphate or sodium perborate having on the surface thereof an organopolysiloxane antifoam agent which is at least partially enclosed within a mixture of a water-insoluble wax having a melting point in the range from above 55°C to below 100°C and a water-insoluble emulsifying agent.

Any organopolysiloxane antifoam agent which is effective in controlling foaming in aqueous media may be employed to prepare the foam control substance used in the compositions of this invention. A variety of such antifoam agents are known and are described for example in U.K. Patent Specifications Nos. 689,306, 859,329, 1,020,022, 1,051,687, 1,051,688, 1,079,832 and 1,110,207. They are normally either viscous paste-like materials or aqueous emulsions. Generally the antifoam agent comprises a polydiorganosiloxane in admixture with from 1 to 10 per cent of its weight of a finely-divided filler having a high (at least 50 square metres per gram) surface area to weight ratio, e.g. a fume or precipitated silica or fume aluminium oxide. The polydiorganosiloxane component usually has a viscosity at 25°C in the range from 50 to 5000 cS. However, polydiorganosiloxanes having viscosity outside this range can be used.

The silicon-bonded substituents in the organopolysiloxane are usually methyl radicals. The organopolysiloxane may, however, also contain other organic radicals, for example, alkyl, alkenyl, aryl, aralkyl and alkaryl radicals such as ethyl, propyl, octyl, tetradecyl, phenyl, benzyl and 2-phenylpropyl, or aminoalkyl radicals as described in U.K. Patent Specification No. 1,050,996. When radicals other than methyl are present they preferably

BEST AVAILABLE COPY

comprise less than about 50 per cent of the total silicon-bonded radicals in the organopolysiloxane.

The polydiorganosiloxanes employed in the antifoam may or may not be end-stopped. Thus they may be terminated for example with hydroxyl radicals or end-stopped with triorganosiloxy radicals e.g. trimethylsiloxy, phenyldimethylsiloxy or dimethylvinylsiloxy radicals.

Preferred for use in this invention are antifoams based on or containing polydimethylsiloxanes and a high (at least 50 m<sup>2</sup>/g.) surface area silica. Among the preferred antifoam compositions are those comprising a mixture of from 80 to 98 per cent by weight of polydimethylsiloxane and from 2 to 20 per cent by weight of a silica having a surface area of at least 50 m<sup>2</sup>/g. Also included in the group of preferred antifoams are those comprising a silica, a polydimethylsiloxane and a polydiorganosiloxane which contains silicon-bonded methyl, ethyl and 2-phenylpropyl radicals, the silica being present in a proportion of from 1 to 10 per cent by weight based on the total weight of polydiorganosiloxane.

In addition to the organopolysiloxane component the silicone antifoam may contain other ingredients, for example resin copolymers of (CH<sub>3</sub>)<sub>3</sub>SiO<sub>0.5</sub> and SiO<sub>2</sub> units as described in U.K. Patent Specification No. 1,110,207.

As the water-insoluble wax there may be employed for example, polyethylene wax, Montan wax, oxidised microcrystal-line wax, carnauba wax, ceresin wax and ozokerite. The wax should have a melting point of above 55°C but below 100°C.

As the water-insoluble emulsifying agent there may be employed, for example, the esters of fatty acids and polyhydric alcohols, e.g. sorbitan monooleate, sorbitan monostearate, ethylene glycol monostearate, glycerol monostearate and polyoxyethylene distearate, and the reaction products of alcohols or phenols, particularly the fatty alcohols, with ethylene oxide, e.g. polyoxyethylene nonylphenyl ether, polyoxyethylene oleyl ether, polyoxyethylene lauryl ether and tallow alcohol ethoxylates, said ethers or ethoxylates containing low proportions of ethoxy groups, usually from about 2 to 5 such groups, per molecule. In general, nonionic emulsifiers with an HLB value below 8 are preferred.

In the foam control substances present in the compositions of this invention the organopolysiloxane antifoam agent is at least partially enclosed in a mixture of the water-insoluble wax and the water-insoluble emulsifying agent. Such an arrangement may be arrived at by mixing the organopolysiloxane antifoam agent and the sodium tripolyphosphate, sodium sulphate or sodium perborate so that the antifoam agent becomes dispersed over the surface of the solid. The treated solid is then contacted with the mixture of water-insoluble wax and emulsifying agent whereby it becomes at least partially encapsulated by said mixture. Any suitable technique may be employed for treating the solid substrate with the organopolysiloxane antifoam agent. For example the antifoam agent, in the form of a thick paste, may be mixed with the substrate using e.g. a ribbon blender to yield a substantially dry and flowable granulate. Alternatively the antifoam agent may be employed in the form of an aqueous emulsion to treat the dehydrated or partially dehydrated substrate. For example dehydrated sodium tripolyphosphate may be contacted with sufficient antifoam emulsion to supply up to six molecules of H<sub>2</sub>O per molecule of sodium tripolyphosphate.

An alternative method of preparing the foam control substance comprises mixing the organopolysiloxane antifoam agent with the wax and emulsifying agent and applying the mixture to the surface of the solid substrate, e.g. the sodium tripolyphosphate. Such application may be carried out by simple mixing of the solid substrate with the other components at an elevated temperature so that the wax and emulsifying agent are molten. The resulting mixture may then be allowed to cool and thereafter crushed. The substrate can also be coated with the molten mixture of organopolysiloxane, wax and emulsifier by containing the powder in a fluidized bed and spray drying the melt onto the fluidized powder mass.

The proportion of organopolysiloxane antifoam agent present in the foam control substance is not narrowly critical and will depend on several factors, including the defoaming effect desired in the detergent composition and the method employed to prepare the foam control substance. Depending on the particular substrate up to about 120 parts of antifoam agent per 100 parts of substrate can be applied to provide a free flowing powder which is then subsequently coated with the mixture of wax and emulsifying agent. When the organopolysiloxane antifoam agent is mixed with the wax and emulsifying agent prior to application to the substrate the proportion of antifoam agent in relation to the other components of the foam control substance can also be varied within wide limits. In general it is preferred that the total amount of wax and emulsifying agent be at least equal to the amount of organopolysiloxane antifoam agent. Preferably the ratio of the total weight of wax and emulsifying agent to the weight of organopolysiloxane antifoam agent is from 1.5/1 to 10/1. The proportion of wax to emulsifying agent can be varied within fairly wide limits but preferably falls within the range from 0.5/1 to 5/1.

The hereinabove described foam control substances are incorporated into powdered or granular detergent compositions in a proportion of from 0.5 to 20% by weight, based on total composition weight, to provide the compositions of this invention. Powdered or granular detergent compositions are well-known and typically contain by weight from 10 to 25 per cent of an organic surface active agent, and about 15 to 50 per cent of an inorganic phosphate e.g. sodium tripolyphosphate. Other ingredients which are normally present include one or more of sodium sulphate, sodium silicate, sodium perborate, foam builders, optical brighteners and perfumes. Typical of the organic surface active agents which are present are sodium salts of alkylaryl sulphonates, sulphates of straight chain primary alcohols, sodium alkyl glyceryl ether sulphonates and sodium and potassium salts of fatty acid mixtures. Specific examples of such organic surface active agents are sodium dodecyl benzene sulphonate, sodium lauryl sulphate and potassium stearate.

The invention is illustrated by the following examples, in which the parts are expressed by weight. The names Brij, Autostar and Omo used in the examples are Trade Marks.

#### Example 1.

Two compositions were prepared. Composition A was obtained by mixing for 3 hours at 175°C a silica (3 parts) having a surface area to weight ratio of about 225 m<sup>2</sup>/g. and a polydiorganosiloxane (97 parts) having a viscosity at 25°C of about 1500 cS, a methyl to silicon ratio of 1:1, an ethyl to silicon ratio of about 0.8:1 and a 2-phenylpropyl to silicon ratio of about 0.2:1. Composition B was obtained by mixing a trimethylsiloxy-terminated polydimethylsiloxane (88 parts) having a viscosity at 25°C of 1000 cS, a silica aerogel (10 parts) and a resin copolymer of (CH<sub>3</sub>)<sub>3</sub>SiO<sub>0.5</sub> and SiO<sub>2</sub> units (2 parts) in which the ratio of the former to the latter units was in the range from 0.6:1 to 1.2:1.

An organopolysiloxane antifoam agent was prepared by mixing together 50 parts of each of Composition A and Composition B. The paste-like product (10 parts) was then mixed with Brij 72 (a stearyl alcohol ethoxylate) (12 parts) and oxidised Montan wax (11.4 parts) at about 80°C. This mixture was tumble mixed while molten with granular sodium tripolyphosphate (66.6 parts) and the mix allowed to cool to yield a granular foam control substance which was free-flowing at room temperature.

10.5 parts of the foam control substance prepared as described above were thoroughly mixed into 98 parts of a heavy duty, granular detergent sold under the trade designation Omo. The mix was stored in a cardboard container under laboratory conditions of temperature and humidity for 4 weeks. In order to evaluate the sudsing properties of the detergent composition portions (108.5 g.) of the composition were taken prior to, during and at the end of the four week storage period. Each portion was evaluated by addition to 28 litres of cold water, hardness 50 ppm Ca++, in a Philips Autostar automatic washing machine calibrated with a 0-17 cm. foam height scale. The maximum foam height achieved during the washing cycle was noted, the wash load consisting of 2 kg. of clean cotton. The results obtained are shown in the following table.

Storage Period	0	1 week	3 weeks	4 weeks
Maximum Foam Height (cm)	13	10	9	10

#### Example 2

The procedure described in Example 1 was repeated except that the foam control substance was prepared from 6.7 parts of the mixture of Compositions A and B, 15 parts of Brij 72, 11.6 parts of oxidized Montan wax and 66.6 parts of sodium tripolyphosphate. This foam control substance was employed in a proportion of 15.75 parts per 98 parts of Omo.

The foam heights obtained initially and after storage for 2 and 4 weeks were 9, 10 and 15 cm. respectively.

#### WHAT WE CLAIM IS:-

1. A powdered or granular detergent composition containing from 0.5 to 20% by weight of a foam control substance which comprises powdered or granular sodium tripolyphosphate, sodium sulphate or sodium perborate having on the surface thereof an organopolysiloxane antifoam agent which is at least partially enclosed within a mixture of a water insoluble wax having a melting point in the range from above 55°C to below 100°C and a water-insoluble emulsifying agent.

2. A detergent composition as claimed in Claim 1 wherein the organopolysiloxane antifoam agent comprises a polydiorganosiloxane in admixture with from 1 to 10 per cent of its weight of a finely-divided silica having a surface area of at least 50 m<sup>2</sup>/g.

3. A detergent composition as claimed in Claim 2 wherein the organic substituents in

the polydiorganosiloxane are methyl radicals.

4. A detergent compositions as claimed in Claim 3 wherein the organopolysiloxane antifoam agent also comprises a polydiorganosiloxane wherein the organic substituents are methyl, ethyl and 2-phenylpropyl radicals.

5 5. A detergent composition as claimed in Claim 3 or Claim 4 wherein the organopolysiloxane antifoam agent also comprises a resin copolymer of  $(\text{CH}_3)_3\text{SiO}_{0.5}$  and  $\text{SiO}_2$  units. 5

6. A detergent composition as claimed in any one of the preceding claims wherein the emulsifying agent is non-ionic and has an HLB value below 8.

10 7. A detergent composition as claimed in any one of the preceding claims wherein the ratio of the total weight of water-insoluble wax and water-insoluble emulsifying agent to the weight of organopolysiloxane antifoam agent is in the range from 1.5/1 to 10/1. 10

8. A detergent composition as claimed in Claim 1 substantially as described with reference to the Examples.

15

W. J. WALBEOFF,  
Chartered Patent Agent,  
Agent for the Applicants.

15

---

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1978.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

BEST AVAILABLE COPY